Carbon Formation in the Steam Reforming Process: a Thermodynamic Analysis Based on the Elemental Composition

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A thermodynamic analysis of the conditions leading to carbon formation on the catalytic bed of methane steam reformers is presented. In the first part of the analysis, a closed system in which steam reforming reactions take place is considered, and elemental compositions leading to carbon formation are determined. In the second part, results of an industrial steam reformer simulation are used to locate, inside the reactor, regions with a positive affinity for coke formation.

1. Introduction

Carbon formation on the reactor’s catalytic bed is a major problem in the methane steam reforming process. Depending on the system conditions, side reactions such as methane cracking or Boudouard reaction may occur at the catalyst surface, leading to carbon deposition in different forms. Carbon may then encapsulate the catalyst surface or dissolve and diffuse inside the catalyst pellet, reducing its activity. The Whisker filamentous form of carbon is particularly noxious, because it can grow inside the catalyst pellet and eventually break it, producing finer particles that alter the fluidodynamics of the reactor.

In order to reduce the risk of carbon formation, industrial steam reformers are fed with gas streams with a steam-to-carbon ratio of about 3, but important economical benefits would be obtained if a lower steam-to-carbon ratio could be used. Therefore, mechanisms and kinetics of carbon formation reactions have been thoroughly investigated (Trimm, 1997; Snoek et al. 2002 ; Ginsburg et al., 2005), with the aim of finding new process configurations that allow for the use of a lower steam content in the feed.

The gas phase inside the reformer is, in general, made of five components (methane, water, hydrogen, carbon monoxide, carbon dioxide), involved in many reactions, thus, it is not easy to define synthetically the conditions that would favour carbon deposition, even limiting the analysis to equilibrium conditions.

In this paper, a thermodynamic analysis based on the elemental composition of the reacting system is presented. In the first part of the analysis, a closed system in which steam reforming reactions take place is considered, and elemental compositions leading to carbon formation are determined. In the second part, results of an industrial steam reformer simulation are used to locate, inside the reactor, regions with a positive affinity for carbon formation.

2. Thermodynamic analysis

2.1 Reactions

Several chemical reactions can take place during the steam reforming process. The most important and thermodynamically probable ones are (Snoek et al., 2003):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{SR}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{DR}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{WGS}$$

$$CH_4 + 2H_2O \leftrightarrow CO + 4H_2 \tag{OSR}$$

and side reactions leading to carbon formation

$$CH_4 \leftrightarrow C + 2H_2 \tag{MC}$$

$$2CO \leftrightarrow C + CO_2 \tag{B}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{RG}$$

It can be easily shown that only 3 out of these 7 reactions are independent, thus, for the following thermodynamic analysis only reactions (SR), (WGS) and (B) will be considered.

Thermodynamic constants for the reactions as a function of temperature have been calulated by ΔH and ΔG of reaction data at 298 K and specific heat $c_p(T)$ of the reactants. Graphite thermodynamic properties have been assumed for carbon.

2.2 Elemental composition

Since the 6 compounds considered contain only C, H and O atoms, the composition of the reacting mixture can be conveniently represented in terms of only 2 independent atomic fractions, defined as the ratio between the number of atoms of one type and the total number of atoms in the mixture. I.e., the hydrogen atomic fraction in the gas mixture is

$$\chi_{\mathrm{H}} = \frac{4y_{\mathrm{CH_4}} + 2y_{\mathrm{H_2O}} + 2y_{\mathrm{H_2}}}{5y_{\mathrm{CH_4}} + 3y_{\mathrm{H_2O}} + 2y_{\mathrm{H_2}} + 2y_{\mathrm{CO}} + 3y_{\mathrm{CO_2}}} \tag{1}$$

where y_i is the mole fraction of compound i in the mixture.

Compared to molar fractions, atomic fractions provide less, but still enough information about the system composition to carry out a thermodynamical analysis of the carbon formation conditions. On the other hand, atomic fractions offer many advantages in terms of simplicity, because they don’t vary with the extent of reaction and allow the composition range corresponding to carbon formation to be synthetically defined.

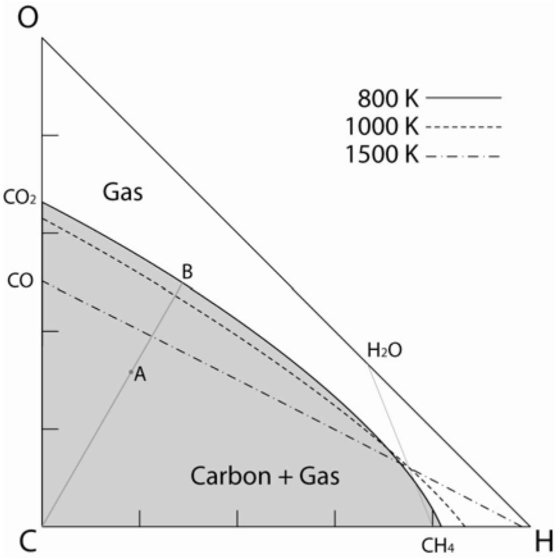


Fig. 1 *Carbon formation conditions on the triangular diagram. The shaded area is the carbon formation zone at 800 K. Limiting curves at 1000K and 1500K are also reported*

2.3 Carbon formation conditions

When carbon is formed, at equilibrium the system is composed of 2 phases, with 6 reactants involved in 3 independent reactions. For such a system, the Gibbs phase rule gives a variance v=3, that is, at given temperature and pressure, the molar fraction of only one compound in the gas phase is independent, while the others may be calculated by the thermodynamic constants of the reactions. Therefore, in the C-H-O plane, the possible equilibrium gas phase compositions lie on a parametric curve of the type

$$\begin{cases}\chi_{\mathrm{H}} = \chi_{\mathrm{H}}(y_i) \\ \chi_{\mathrm{O}} = \chi_{\mathrm{O}}(y_i)\end{cases} \tag{2}$$

where y_i is the molar fraction of one of the gaseous reactants. Fig. 1 shows the equilibrium curves obtained at different temperatures for a pressure of 15 atm. At high temperature, all the reactions are shifted towards the formation of CO and H_2, thus, the equilibrium curve tends to the line joining the points representing these compounds.

The equilibrium curve divides the triangular diagram in two regions (fig. 1):

- **CARBON+GAS**: systems in this region (i.e., point A), at equilibrium are constituted of a carbon solid phase (point C) and a gas phase (point B).
- **GAS**: systems in this region are homogeneous at equilibrium and no carbon is formed

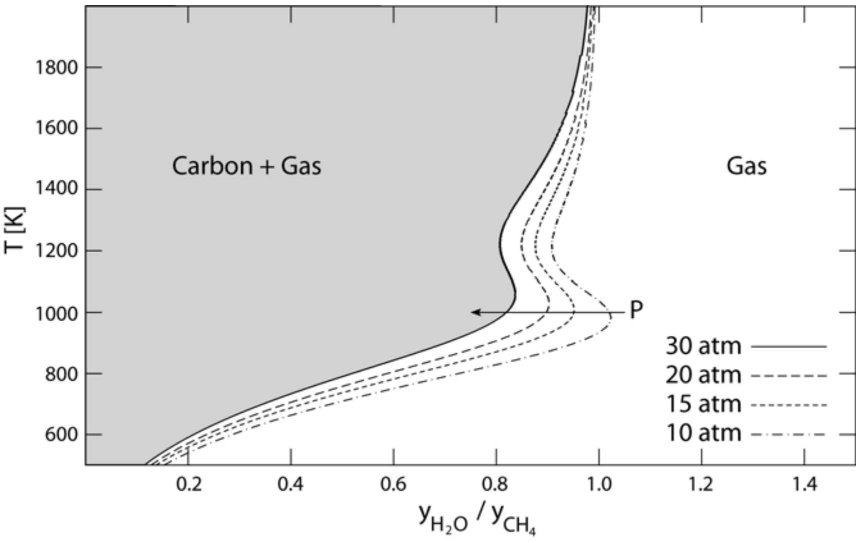


Fig. 2 *Carbon formation conditions for a steam–methane system. The shaded area is the carbon formation zone at 30 atm. Limiting curves at different pressures are also reported.*

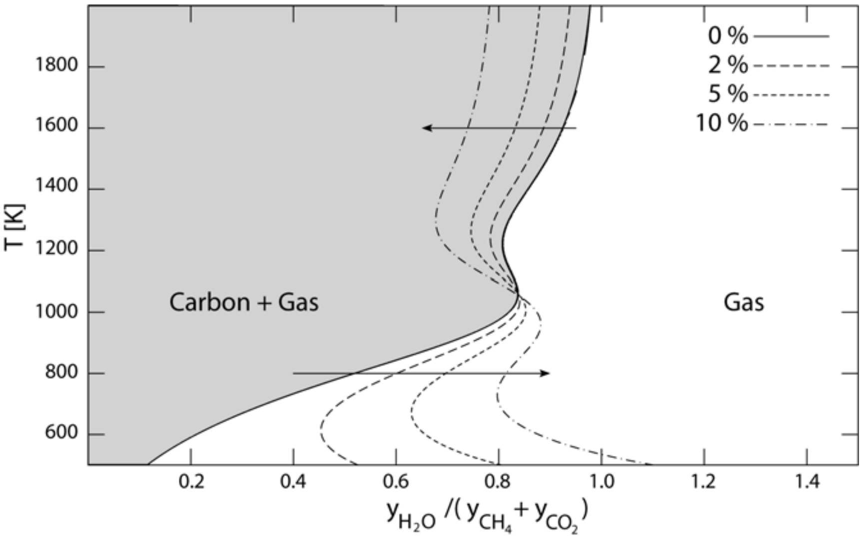


Fig.3 *Carbon formation conditions for a steam-methane-carbon dioxide system at 30 atm. The shaded area is the carbon formation zone when no carbon dioxide is present. Limiting curves at different* $y_{CO_2}/(y_{CO_2}+y_{CH_4})$ *are also reported.*

2.4 Steam - methane systems

Steam reformer feed is mainly composed of steam and methane, thus a particular focus must be put on elemental compositions lying on the line that joins H_2O and CH_4 points.

The equilibrium curve intersects this line in a point whose position depends on the system temperature and pressure (fig. 1). This point corresponds to a minimum value of the y_{H2O}/y_{CH4} ratio (steam-to-carbon ratio), below which, at equilibrium, carbon will be produced.

In fig. 2, the limiting conditions are plotted in a temperature vs. steam-to-carbon ratio plane, for different system pressures: points on the left of the curve represent conditions in which carbon is formed. It can be noted that higher pressures slightly reduce the possibility of carbon formation at all temperatures and that for high temperatures the limiting steam-to-carbon ratio tends to 1, that is far below the value of 3 are used in the industrial practice.

2.5 Steam - methane - carbon dioxide systems

Actual steam reformer feed contain other components such as carbon monoxide and carbon dioxide, that, even if present in small quantities, increase the carbon content of the system and can change significantly the coking limits. Furthermore, the analysis could also be applied to the methane dry (CO_2) reforming process, in which carbon dioxide is one of the main feed components.

Therefore, in order to give a first evaluation of the effect of other carbon sources, the feed was assumed as a mixture of water, methane and carbon dioxide. Fig. 2 shows how the CO_2 affects the coking limits. The effect is different depending on the temperature: at high temperatures (>1000 K), the presence of CO_2 reduces the carbon formation zone, while for low temperatures the opposite effect is observed.

Again, a steam-to-carbon ratio of 3 is far away from the carbon formation conditions.

2. Affinity for coke formation in a fixed bed reactor

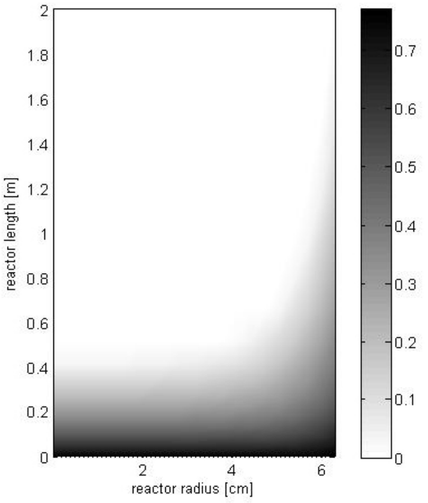
An exhaustive study on the carbon formation conditions can not be limited to the previous analysis of equilibrium conditions. Considering a fixed bed reactor, local compositions must also be checked to see if, in some points of the reactor, any side reactions can thermodynamically proceed toward carbon formation.

To this aim, it is useful to define the *affinity* of each carbon forming reaction as follows

$$a_i = 1 - \frac{\pi_i}{K_i} \tag{3}$$

where K_i is the thermodynamic constant of the *i*-th reaction and $\pi_i = \Pi_j p_j^{\nu_{ji}}$, where p_j is the partial pressure of component j in the reacting mixture and ν_{ji} is its stoichiometric coefficient in reaction *i*. It can be stated that, when a_i is defined in a point of the reactor and $0 < a_i \leq 1$, carbon will be produced by reaction *i* in that point.

In order to locate the critical regions for carbon deposition, simulations of a steam reformer (length 12 m, internal diameter 12.6 cm) were carried out using a steady-state, bidimensional model (De Falco et al., 2007). The temperature, pressure and composition distributions obtained were subsequently used for affinity calculation.



Inlet stream conditions:

Temperature:	793 K
Pressure:	3.03 MPa
Molar flow-rate:	25.7 kmol/h
Molar composition:	
CH_4	31.15 %
H_2O	62.30 %
H_2	4.68 %
CO	0.31 %
CO_2	1.56 %

Fig. 4 *Affinity (eq. 3) for carbon formation by (MC) reaction in a fixed bed steam reformer. Inlet stream conditions are reported next to the figure.*

It must be pointed out that the model used doesn’t take into account carbon forming reactions: this approach is based on the reasonable hypothesis, also assumed by Snoek et al. (2003), that carbon formation has a negligible effect on mass and energy balances inside the reactor.

Fig. 4 shows a shade plot of carbon formation affinity of reaction (MC), which, at the conditions of the simulation, is the most important carbon formation reaction among those considered. For the sake of clarity, only positive values of affinity have been plotted, while negative affinities are plotted as zero. The plot is limited to the first 2 m after the catalytic tube entrance, because a positive affinity for carbon formation is obtained only in the first layers of the catalytic bed.

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